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(71) Applicant : **THE MEAD CORPORATION**
Mead World Headquarters Courthouse Plaza Northeast
Dayton Ohio 45463 (US)

(72) Inventor : **Austin, Robert A.**
651 Deauville Drive
Dayton, Ohio 45429 (US)
Inventor : **Rising, Paul E.**
2820 Hickorywood Drive
Troy, Ohio 45373 (US)
Inventor : **Shackle, Dale R.**
2481 Pennyroyal Road
Springboro, Ohio 45066 (US)
Inventor : **Bionsky, Peter M.**
1225 Smugglers Way
Centerville, Ohio 45459 (US)

(74) Representative : **Deans, Michael John Percy et al**
Lloyd Wise, Tregear & CO. Norman House
105-109 Strand
London WC2R OAE (GB)

(54) Coated product, and methods for providng a coated substrate or for forming a printed substrate.

(57) A layer of a coating composition is coated on to at least one surface of a continuous web of a planar substrate as said web is moved past a coating means. The coating composition is radiation or thermally curable, contains less than about 5% solvent or water and contains at least about 60% pigment based on the weight of said composition. The surface of the said layer is formed and the coating composition is at least partially cured.

EP 0 485 240 A1

The present invention relates to coated products. Particular aspects of the invention are concerned with the provision of a coated substrate and with the formation of a printed substrate.

It is well known in the paper industry that some of the smoothest and highest quality coatings can be formed by cast coating. A number of processes exist in which a coating may be applied to a sheet or substrate, contacted with a casting surface, cured, and separated from the casting surface. In one casting process, a resinous material, such as polyvinyl chloride or polyurethane resin, in a flowable state is deposited or formed onto a casting surface, irradiated, and cured so that the resinous material may be separated from the casting surface to thereby effectively replicate the casting surface. Several irradiating techniques have been employed to cure such coatings, for example, UV irradiation, electron beam irradiation and thermal irradiation.

U.S. Patent Nos. 4,246,297, 4,252,413 and 4,521,445 disclose electron-beam curing materials using electron-beam irradiation.

U.S. Patent No. 4,322,480 discloses a method of providing surface replication in a release coating on a substrate which comprises the steps of applying a coating of an electron beam radiation curable composition or material directly to one side of a web of coated paper, pressing the coated side of the substrate against a replicative surface, sufficiently irradiating the coating through the substrate to partially cure the coating yet enable removal from the replicative surface, irradiation taking place after coating has penetrated into the coated paper and is in continuous intimate contact with the coated paper, and stripping the substrate from the replicative surface with at least partially cured coating adhered to the substrate. The patent teaches press roll coating a substrate with a coating composition including a moderate molecular weight (300 to 800 g./mole) functional oligomer; a reactive monomer diluent (a mono or multifunctional acrylate or methacrylate) such as trimethylolpropane triacrylate (TMPTA) or isodecyl acrylate; pigments or fillers such as clay, silica or diatomaceous earth, reactive or non-reactive silicones, and organic diluents (solvents) such as acetone or carbon tetrachloride. The coating composition has a viscosity less than 1300 cps.

U.S. Patent No. 4,364,971 discloses a method for producing a waterproof photographic paper support by coating a surface of photographic base paper with a pigment-coating resin hardenable by irradiation, pressing the resin coated surface against a substantially solid high gloss surface, irradiating with electron beam irradiation to substantially completely harden the resin while in contact with the high gloss surface, and separating the substantially completely cured coated surface from the high gloss surface to form a waterproof paper support having a surface smoothness of at least 70% that of an ideal mirror surface, as measured by an image reflected from the hardened, coated surface. The patent teaches applying the coating with a rotating cylinder and the thickness being controlled by a doctor blade. The coating composition includes a binder (polymerizable compound) and pigment. The pigment concentration in the coating composition is limited to 45% by weight of the coating composition.

In the manufacturing of a paper board or paper support for use in packaging or the like, it is often desirable that the support be able to take on a high quality print or decorative finish. In an attempt to achieve this result, the support may be coated with a water-based composition which contains a binder and pigment.

An inorganic white pigment can be employed for forming a white pigmented surface. It would be particularly desirable to have a high concentration of pigment, in excess of 50% by weight of the coating composition, in a coating material to obtain a high quality printing surface.

Previous attempts to coat a substrate using a coating composition having an amount of inorganic pigment in excess of 50% by weight of the coating composition have resulted in several problems. Due to extremely high viscosity of such compositions, conventional application techniques rely upon solvents to descrease the viscosity of the coating composition. Evaporation of solvent causes cracking or faults in the surface of the coating. Also, solvent (water) wets the substrate and can cause swelling of the substrate and shrinkage of the coating during drying. Solvents also pose potential fire and toxicity hazards; thus, there is a need for a substantially solvent-free coating composition.

The present invention arises from our work in seeking to overcome the above problems and provide a method for providing to a substrate a high quality surface.

In accordance with a first aspect of the present invention, there is provided a method for providing a coated substrate comprising the steps of:

(a) providing a radiation or thermally curable coating composition containing less than about 5% solvent or water and containing at least about 60%, and preferably at least about 70%, pigment based on the weight of said composition;

(b) coating a layer of said coating composition on to at least one surface of a continuous web of a planar substrate as said web is moved past a coating means;

(c) forming the surface of said layer; and

(d) at least partially curing said coating composition.

In a second and alternative aspect thereof, the invention provides a coated product comprising a substrate

having a layer of a coating cured on a surface thereof; characterised in that said cured coating is the result of curing a composition containing less than about 5% solvent or water and from about 70-85% pigment based on the weight of said coating composition, and in that said cured coating has a Sheffield smoothness less than 25. We have found such coated products to be excellent for printing thereon.

Examples of our product provide a high gloss and open or absorptive surface.

According to a further and alternative aspect of this invention, there is provided a method for forming a printed substrate which comprises the steps of:

(a) providing a radiation or thermally curable coating composition containing less than about 5% solvent or water and containing at least about 60%, and preferably at least about 70%, pigment based on the weight of said composition;

(b) coating a layer of said coating composition on to at least one surface of a continuous web of a planar substrate as said web is moved past a coating means;

(c) forming the surface of said layer;

(d) at least partially curing said coating composition, and

(e) applying a printing ink to the surface of said layer.

The invention is hereinafter more particularly described by way of example only with reference to and as shown in the accompanying drawings, in which:-

Fig. 1A is a schematic illustration of a process for coating a substrate with a high quality surface having a radiation or thermally cured coating wherein a drum casting surface is used;

Fig. 1B is a schematic illustration of a process for coating a substrate with a high quality surface having a radiation or thermally cured coating wherein the casting surface is a film or foil;

Fig. 1C is a schematic illustration of a process for coating a substrate with a high quality surface having a radiation or thermally cured coating; and

Figs. 2A and 2B are pictures depicting surface smoothness of examples of our coated substrates as compared to conventional coated substrates.

The terms "form the surface" and "forming the surface" and variations thereof are used herein to mean to simply smoothen the surface of the coating or to cast coat the surface.

As described hereinbelow, coating compositions employed in practice of the present invention contain a vehicle and a pigment. The vehicle is a radiation or thermally curable material. A preferred example is an electron beam curable material. Suitable vehicles include resins and prepolymers containing one or more ethylenically unsaturated carbon double bonds per molecule which can be hardened by radiation such as acrylates, methacrylates, vinyl pyrrolidinones, acrylic esters of aromatic or aliphatic polyurethanes, acrylic esters of terephthalic acid-diol polyesters, acrylic esters of methylol melamine resins, maleic acid diol polyester, acrylic esters of bisphenol A epoxy resins, unsaturated polyester resins, allyl ethers, styrene-butadiene copolymer resins, acrylic acid esters of hydrolyzed starch or hydrolyzed cellulose, fumaric acid diol polyester. Suitable monomers which can be hardened by electron beam radiation are acrylic acid esters of monohydric or polyhydric alcohols,methacrylic acid esters of monohydric or polyhydric alcohols, acrylic acid esters and methacrylic acid esters of ether alcohols, monofunctional acrylates or methacrylates, multifunctional acrylates or methacrylates of polyfunctional alcohols, cyanoethyl acrylates glycidyl(meth)acrylate, allyl acrylate, cyclohexylmethacrylate, diallyl fumarate, divinylbenzene, vinyl toluene. The above list of radiation curable materials is not meant to be limiting and it is within the scope of this invention that other suitable materials may be used.

Certain photospeed enhancing additives can be included in the coating composition to enhance the rate of cure and thereby improve productivity, or to reduce radiation dosages and thereby reduce any weakening of the substrate by the radiation. One particularly advantageous additive is N, N-dialkylanilines and more particularly diisopropyldimethylaniline (DIDMA), 6-ethoxy-2-mercaptobenzothiazole and other thiols.

Representative examples of N,N-dialkylanilines useful in our compositions are 4-cyano-N, N-dimethylaniline, 4-acetyl-N, N-dimethylaniline, 4-bromo-N, N-dimethylaniline, ethyl 4-(N,N-dimethylamino) benzoate, 3-chloro-N,N-dimethylaniline, 4-chloro-N,N-dimethylanile, 3-ethoxy-N,N-dimethylaniline, 4-fluro-N,N-dimethylaniline, 4-methyl-N,N.-dimethylaniline, 4-ethoxy-N,N.-dimethylaniline, N,N-dimethylthioanicidine, 4-amino- N,N-dimethylaniline, 3-hydroxy-N,N,-dimethylaniline, N,N,N',N'-tetramethyl,4-dianiline, 4-acetamido-N, N-dimethylaniline, etc. Preferred N,N-dialkylanilines are substituted with an alkyl group in the ortho-position and include 2,6-diisopropyl-N, N-dimethylaniline. 2,6-diethyl-N,N.-dimethylaniline, N,N,2,4,6-pentamethylaniline (PMA) and p-t-butyl-N,N.-dimethylaniline.

The N,N-dialkylanilines are preferably used in our compositions in concentrations of about 0.1 to 4% by weight. Other speed enhancing additives are used in equivalent amounts.

A vehicle composition is selected which provides the optimum combination of smoothness, coating adhesion and resistance to cracking and flaking for a particular end use. For example in making coated board for containers, because the board is bent in use, the coated layer should not crack on bending. In making printing

or text paper, this is also important but to a lesser degree. The amount of any crosslinking monomer or oligomer is adjusted to provide the desired degree of hardness or elasticity in the coating. For coated board a softer layer is desired. For publishing paper, a harder and more rigid coating may be used. Urethane backbones impart flexibility to a polymer. Mono-functional monomers, because they do not crosslink, generally produce a more flexible coating. To increase solvent resistance and stiffness, di- and tri-acrylates are added. The proportion of these differing functionalities is varied along with the monomer backbone to control the final properties of the coating.

Another characteristic that is controlled by the monomer composition and monomer proportions is the fluidity and ability of the coating composition to wet and penetrate the substrate. Since it is necessary that the coating adhere firmly to the substrate, the vehicle must penetrate the substrate to bond to it. If composition is too fluid, it will soak in rapidly, leaving the pigment behind resulting in chalking and higher coat weights may be required. If it is too viscous, it will not soak in sufficiently and not adhere to the substrate.

Materials may be dissolved in the vehicle to control the viscosity. For example, oligomers, or polystyrene or other polymers may be added to increase the viscosity of the vehicle mixture. Plasticizers may decrease the viscosity of the vehicle, impart flexibility and toughness to the resulting polymer and enhance the ink absorptivity of the coating.

One particularly preferred coating composition includes nonylphenol ethoxylated monoacrylate, aliphatic urethane acrylate and polyethylene glycol diacrylate.

The vehicle is employed in the composition in an amount of about 15-40% by weight based on the total composition and preferably of an amount from about 20 to 25% by weight based on the total composition.

A variety of substrates may be coated in accordance with the teaching herein to provide a variety of different products. Substrates which can be used in practicing the present invention include paper, paperboard, wood, plastic, ceramic, textiles or metal. Examples of substrates are rawstocks such as the rawstock for the cast coated or offset enamel papers sold by The Mead Corporation under the MARK I, MARK IV and SIGNATURE trademarks. Examples of these rawstocks may be 57 pound (25.9 Kg), 104 pound (47.2 Kg) or 117 pound (53.1 Kg) per book ream. To reduce coat weight it may be desirable to precoat a substrate with a coating of a polymer such as E-960 from Borden Co. or to pre-coat a layer of polymer and a pigment such as calcium carbonate or clay.

Coated or uncoated natural Kraft board such as Mead's CNK and NK 18 point and 21 point board may be coated with the compositions and the processes described herein. Photographic basestock (130-140 pound/59-63.5 Kg) and a 40 pound (18.1 Kg) rawstock known as "label stock" because it is used in making labels are also useful herein as are papers made from recycled paper fibers. Among other products which can be made using these substrates are fine cast coated papers, white board, container board and photographic papers. Coated substrates as described herein are particularly advantageous because they provide a very high quality printing surface. However, they are not necessarily printed. Whiteboard can be used unprinted to prepare boxes.

Pigments generally employed in practice of our methods are inorganic or plastic pigments and preferably white inorganic pigments. Suitable white inorganic pigments are barium sulfate, titanium dioxide, calcium carbonate, zinc sulfide, metal silicates, magnesium oxide, aluminium oxide and hydroxide, mixed oxides of titanium, titanium phosphate, satin white, silicon dioxide, zinc oxide, clay, zirconium oxide, and tin oxide. Pigment concentration used is generally of a very high percent, ranging from 60 to 85%, and preferably from about 70 to 80%, based on the total weight of coating composition.

Typical polymerized vehicle has a refractive index of about 1.4, where refractive index is the ratio of the speed of light in air to that in the vehicle. In order for the pigments to give good opacity, it is desirable that the pigment used have a refractive index differing from 1.4. Thus, for example, calcium carbonate or clay pigments have an index of refraction similar to that of most polymerized vehicles and contribute little to the opacity of the coating but are generally employed for their absorptive properties where high opacity is not necessarily required. For coating brown board substrates, preferred pigments have an index of refraction of approximately 2 or greater in order to give higher opacity. Titanium dioxide has an index of refraction of 2.3 to 2.5, depending upon the crystalline type, and is an excellent pigment for obtaining good opacity. Some pigments may be transparent to ultraviolet light, in which case sensitizers can be added to the coating composition before UV irradiating.

Pigments may be coated to enhance dispersibility and lower viscosity. Suitable coatings for pigments are hydrous $Al(OH)_3$ or Al_2O_3 and hydrous silicon dioxide. Pigments may also be coated with an oleophilic, hydrophobic or an organic coating, such as B-diketone chelate or polyvinyl alcohol, to enhance dispersibility and decrease viscosity. Titanium dioxide, for example, is commercially available with organic coatings which enable its use in higher amounts in coating compositions. One such coated titanium dioxide is RCI-4 from SCM Corp. Since, the coating composition is thixotropic, the thixotropy can be reduced with coated pigments

because the coating, for example, is much more compatible with the organic liquid than the highly polar, uncoated pigment.

A three roll mill may be used to mix the coating composition. Alternatively, a high speed dispersing mill may be used, such as the mill made by Bowers Manufacturing.

The viscosities of the coating compositions employed in our methods are generally above 10,000 cps and typically about 10,000 to 60,000 cps but can range as high as 100,000 to 2,000,000 cps. Unless otherwise indicated, the viscosities reported herein are at room temperature and low shear (7 sec^{-1}).

While the coating compositions used are relatively viscous, they are thixotropic and their viscosity reduces under shear and with heating. Even though the coating composition may have a high viscosity at rest or when sheared little, the shear at the coating head is very high, resulting in greatly reduced viscosity. This shear thinning (decrease in viscosity) at the coating head makes it possible to coat a material of apparently prohibitively high viscosity. Viscosity at the coating head typically can be as low as 30,000 cps and is preferably lower than 10,000 cps.

Typically, the high solids coating composition is applied to the base stock by extrusion or offset gravure. Other coaters such as blade coaters, direct gravure, knife coaters, roll coaters, etc. may also be useful. Due to its high solids content, the coating composition does not readily form a film that shows substantial cohesion as coated. Coating conditions such as rate of extrusion, gap distance and web speed must be appropriately set or a skip or low spot may be formed in the coating. The coating composition is extruded in direct contact with the substrate or it is applied to the substrate by offset gravure.

Additional components may be added to the composition. For example, antioxidants and UV absorbers may be added. Release agents such as waxes, fatty acids, soaps or silicones, can be employed to improve release from the casting surface. A particularly preferred release agent which can be used is Dow Corning Additive 57 or additive HV-490 which are silicones.

A particularly desirable additive to the coating formulation is a non-ionic surfactant which functions in two ways: first, to ensure release of the coating composition from the casting surface, and second, to enhance ink absorptivity. The coating compositions are essentially non-porous. The surfactant plasticizes the coating and makes it receptive to water based and solvent based inks. A particularly preferred plasticizer is a polypropylene oxide-polyethylene-oxide (PPO-PEO) block copolymer such as Pluronic-L64 which is commercially available from BASF Co.

Colourants and/or opacity enhancers may be used to increase opacity or tint the coating composition. Such colourants or enhancers include carbon black, Phthalocyanine Blue, Disperse Red, Blue or Brilliant Green and hollow glass or plastic beads.

Dispersants can be utilized to improve dispersion of pigments by increasing both particle separation and reducing viscosity. They can be added to the composition or coated on the pigment colour ant or additive solid. Polyvinyl alcohol is a particularly preferred dispersant.

The coating composition can be non-aqueous, solvent-free or may contain small amounts of solvent or water. Typically, base stocks contain up to 5% water and, as such, up to 5% water can be present in the coating without a need to dry the composition and without shrinkage of the underlying substrate.

Referring now to FIG. 1A, a process for coating is shown. For higher viscosity compositions, coating composition 10 is placed into a pump or ramming apparatus 12. Ramming apparatus 12 is capable of exerting high pressures to about 1000 psi ($6.89 \times 10^6 N/m^2$) on coating composition 10, thereby causing coating composition 10 to move through conduit 14. Coating composition 10 can be directly pumped through metering pump 16, wherein coating composition is ultimately moved through conduit 18 and out extrusion head 20.

Web 22 is positioned adjacent extrusion head 20 such that web surface 24 passes extrusion orifice 26. Back-up roller 28 is adjacent orifice 26 and juxtaposed opposite surface 30. Extrusion head 20 has stabilizing bars 32 and 34 and back-up roller 28 has stabilizing bar 36. Stabilizing bars 32, 34 and 36 are present to fix a gap of predetermined width between head 20 and back-up roller surface. Stabilization is necessary to obtain uniform smooth coating due to the high viscosity and low binder content of coating composition 10. If the gap is too large, coating composition 10 will form noncontinuously upon web surface 24 because coating composition is of a low cohesive nature.

Since coating composition 10 is so viscous, hydrodynamic pressure build-up occurs between the extrusion head 20 and web 22. Therefore, extrusion head 20 and back-up roller 28 may be designed to provide a uniform thickness of coating composition 10 yet allow for slight web thickness variation to avoid breaks in continuity of coating composition 10 when applied to surface 24.

Extrusion head 20 can be a T-type extrusion die or a coat hanger type extrusion die and includes trailing lip 40 integrally formed thereon and which provides a surface which uniformly smooths coating composition 10 onto web surface 24. Trailing lip 40 has virtually no flexibility. Trailing lip 40 may be slightly arcuate or a straight edge, but must be without defect as any defect in lip 40 will be replicated in web surface 24. Lip 40 should be

adjusted to obtain maximum smoothness.

In addition to extrusion head 20 and trailing lip 40, flexible blade 41 may be used to smooth the coating after trailing lip 40. Flexible blade 41 may be straight or bent. Its function is to smooth small irregularities in the surface and not to move large quantities of the coating. If a streak or bubble is present, flexible blade 41 will level the surface so the streak or bubble is removed. In some cases, blade 41 is substantially separated from trailing lip 40, and smoothing is done on the already substantially level surface. In other cases, blade 41 and lip 40 may be so close that there is excess coating material between the two and smoothing is done by the flexible blade from a puddle of coating material. It is important that flexible blade 41 have a smooth trailing edge because a small burr in its trailing edge will cause a streak.

Back-up roller 28 may be of a metal, plastic, or elastomeric material. As mentioned, uneven thickness of web 22 may lead to hydrodynamic pressure build-up since the gap is fixed. Therefore, a hard elastomeric material is preferred in order to accommodate slight variations in thickness of web 22 and reduce hydrodynamic pressure.

As those skilled in the art will appreciate, coating thickness on web surface 24 is a function of the gap distance between head 20, web surface 24 and the speed at which web surface 24 passes orifice 26, and the rate of extrusion of coating composition 10. Coating rates can range from 3 to 4000 feet per minute (fpm) (0.9144 to to 1219.2 m/minute). Coating weight ranges from about 7 to 200 grams per square meter (gsm) with a preferred range from 15 to 100 gsm is desired in order to give good opacity and print quality. To obtain optimum smoothness, extrusion head 20 should be 5-15 microns above the highest points of web surface 24. Once the gap distance and the web speed are set, it might be desirable to adjust the extrusion rate slightly in order to assure a complete coating on web surface 24 without waste.

In accordance with the preferred embodiments of the present invention, web 22 with coating composition 10 thereon may be casted by drum 42, as depicted in FIG. 1A; or alternatively, web 22 with coating composition 10 thereon may be casted by film 44, as shown in FIG. 1B. In the case where no cast coating is desired as shown in FIG. 1C, trailing lip 40 and flexible blade 41 may be adjusted to provide a smooth surface.

It is also understood that coating composition 10 can be applied to both surfaces of web 22 if desired. For example, web 22 can be coated on one surface, rolled up, and then unrolled in a manner to allow the other surface to be coated.

Coating composition 10 may be cured thermally or through ultraviolet or electron beam irradiation. In the case of electron beam irradiation, electron beam 46 is depicted as being capable of irradiating through web 22 in order to substantially cure coating composition 10 to thereby replicate surface 48 of drum 42, as shown in FIG. 1A. Electron beam curing on a drum is generally disclosed in U.S. Pat. Nos. 4,521,445 and 4,322,450, the disclosures of which are to be regarded as effectively incorporated herein by reference. In FIG. 1B, electron beam 46 is positioned above film 44 and is capable of irradiating through film 44 to substantially cure coating composition 10 to thereby finish surface 50 of film 44. Alternative embodiments may include the case wherein electron beam 46 is located within drum 42 to cure coating compositions 10 through surface 48 of drum 42, or where in FIG. 1B electron beam 46 is located such that it is capable of irradiating through web 22 to substantially cure coating composition 10 while in contact with film 44. It is also comprehended by the present invention that electron beam 46 could be an ultraviolet irradiation source or thermal source.

As depicted in FIGS. 1A and 1B, radiation source 52 may also be used to partially cure coating composition prior to casting, or as in FIG. 1C where no casting surface is desired, radiation source 52 may be used to substantially cure coating composition 10. Where no casting is desired, trailing lip 40 can be adjusted to provide a substantially smooth surface which can subsequently be cured by the above techniques.

Guide rolls 54 and 56, and 58 and 60, can be employed for conducting the web drum coating composition 10 in contact with drum surface 48, and film surface 50, respectively.

Roller 42 may be composed of either a metal, plastic or rubber roller. Film 44 may consist of a metal or plastic film. In the processes depicted in FIGS. 1A and 1B, after coating composition 10 is substantially cured by electron beam 46, coating composition 10 can be separated from roll 42 or film 44.

The amount of irradiation necessary to substantially cure coating composition 10 is a function of whether or not coating composition 10 is directly or indirectly irradiated, and if indirectly, the density and thickness of the material which must be penetrated in order to reach coating composition 10. The coating composition 10 is substantially cured when further irradiation or curing will cause little change in the character of coating composition 10. Coating composition 10 is partially cured when composition 10 is partially polymerized and will flow under pressure whereas a substantially cured composition 10 will not flow without damaging web 22. As thickness and density of composition 10 increases, irradiation intensity time must also increase. Also, as substrate thickness increases, irradiation intensity must increase. For example, irradiating through a 4 to 5 mil (1.016×10^{-4} to 1.27×10^{-4}m) substrate having a density of 1 gram per cubic centimeter would require an electron beam power of approximately 175 kilovolts (kV), irradiating through 10 mils (2.54×10^{-4}m) would require approxim-

ately 200 kV, irradiating through normal paper stock under 18 mils (4.572×10^{-4}m) would require approximately 300 kV and irradiating a paperboard stock of approximately 26 mils (6.604×10^{-4}m) would require about 450 kV in order to cure coating composition 10.

A casting surface may be used to form a smooth surface, but may not be as effective as other means for smoothing a surface. For example, trailing lip 40 and flexible blade 41 can be adjusted to provide a substantially smooth surface and radiation source 52 can be used to substantially cure coating composition 10 subsequent to extrusion of coating composition 10 onto web 22.

Once the coating composition was cured, it was measured for smoothness under both Sheffield smoothness and Parker Print surface tests. These tests measure the amount of air leaking from the center of a flat, round surface. A rough surface allows more air to leak out than a smooth surface, and low values indicate a smooth surface.

The following examples are intended to show the superiority of examples of the present process and products produced by the methods hereof, but are not intended to be limiting to the details thereof.

Example 1

Material	Commercial Source	Parts
Acrylated ethoxylated linseed oil	Henkel Photomer 3082	17
Ethylhexyl acrylate	Aldrich	8
Titanium dioxide	SCM Corp. Tiona RGM	18
Calcium carbonate, ground	Omyacarb PG3	57

The acrylates were mixed together overnight in a three roll mill, mixing the extremely viscous and very fluid liquids. The remaining materials were combined together using a mortar and pestle. The resulting materials were then milled together in the roll mill, resulting in good dispersion. The viscosity showed some shear thinning, with viscosity dropping from 200,000 cps at 7 sec^{-1} to 120,000 cps at 57 sec^{-1}.

The composition was blade coated on CNK board (a product of The Mead Corporation) and film cast as shown in Fig. 1b.

Example 2

Materials	Commercial Source	Parts
Nonylphenol ethoxylated monoacrylate	Henkel Photomer 4003	9.7
Aliphatic urethane acrylate	Henkel Photomer 6230	12.7
Polyethylene glycol diacrylate	Sartomer 344	2.6
Titanium dioxide	SCM Corp. Tiona RCL-4	35
Calcium Carbonate	Omyacarb FT	40
Carbon	Shawinigan Black	.005

The three acrylates were mixed together easily with light mixing. The remaining materials were mixed using a mortar and pestle and then added to the acrylate in a three roll mill, resulting in excellent dispersion. Mixing can alternately be done in a high speed dispersing mill made by Bowers Manufacturing. The product is highly thixotropic, with viscosity of 250,000 cps at 7 sec^{-1}, low shear, which drops to 20,000 cps at 240 sec^{-1}, higher shear. It takes a few minutes for the viscosity to rise to the original when high shear is removed.

This viscosity characteristic is especially desirable for coating since the coating head has high shear at

the moment of application. With the resulting low viscosity, the coating can be easily smoothed and some self-leveling of the coating occurs. Once application is complete, the viscosity increases as reflected by the thixotropic character.

The composition was blade coated onto CNK board. Three samples were prepared: one in which the coating was blade coated without cast coating; one in which the coating was cast coated using a film as shown in Fig. 1b and one in which the coating was cast coated using a drum as shown in Fig. 1a.

The following Table shows a comparison of smoothness between various substrates. Sheffield Smoothness and Parker Print Surface smoothness tests were done on the substrates in order to determine the smoothness of the surface of the substrates, wherein low values indicate a smoother surface. As can be seen from the Table, Examples 1 and 2 coating composition gave much smoother surfaces than Coated Natural Kraft. Example 2, which was cast on a drum, is the smoothest surface.

SMOOTHNESS COMPARISONS TABLE

Material	Sheffield	Parker
Polypropylene film	0	0.6
Cast Coated Rawstock	120	7.8
Cast Coated Cover	31	1.0
Mead Offset Enamel[1]	13	1.3
CNK Rawstock	360	12.2
CNK Rawstock+Blade Coat	220	5.9
CNK Product	230	3.1
Example 1, Cast on Film	80	1.8
Example 2, Head Smoothed	55	1.1
Example 2, Cast on Film	20	0.5
Example 2, Cast on Drum	0	0.5

[1] Mead Offset Enamel is a coated text printing paper grade.

Example 3

Materials	Commercial Source	Parts
Nonylphenol ethoxylated monoacrylate	Henkel Photomer 4003	7.8
Aliphatic urethane acrylate	Henkel Photomer 6230	8.0
Polyethylene glycol diacrylate	Sartomer 344	4.2
Titanium dioxide	SCM Corp. Tiona RCL-4	35.0
Calcium Carbonate	Omyacarb FT	45.0

Example 3 was mixed in a similar manner to that of Example 2.

Example 4

Materials	Commercial Source	Parts
Nonylphenol ethoxylated monoacrylate	Henkel Photomer 4003	6.63
Aliphatic urethane acrylate	Henkel Photomer 6230	8.63
Polyethylene glycol diacrylate	Sartomer 344	1.74
Titanium dioxide	SCM Corp. Tiona RCL-4	35.0
Calcium Carbonate	Omyacarb FT	48.0

Example 4 was mixed in a similar manner to that of Example 2.

Example 5

Materials	Commercial Source	Parts
Acrylated ethoxylated linseed oil	Henkel Photomer 3082	30.0
Urethane monoacrylate	Henkel Photomer 6173	30.0
Calcium carbonate	Omya Hydrocarb PG-3	120.0
Benzophenone	Aldrich Chemical	1.0

The above materials were mixed together in an aluminum weighing pan, making a viscous mass. The mixture was coated on bond paper and covered with Polyethylene Terepthalate (PET) film. After exposure to an ultraviolet light (American Ultraviolet Co., Porta-cure 1500 watt) for 6 seconds on both sides, the sample was cured and the PET removed to make a shiny coating on the paper.

Example 6

Using a procedure similar to Example 5, the following composition was mixed, cast coated onto a support and cured by exposure to electron beam:

Material	Amount (parts)
Tripropylene Glycol Diacrylate	3.5
Trimethyloprane triacrylate	4.0
Urethane acrylate (Henrel polymer P-6230)	3.0
Nonyl Phenol methoxylated acrylate (Henkel P-4003)	5.2
DIDMA	0.3
Inhibitor (Q-1301)	0.125
RCL-4 (coated TiO_2)	35
PG-3 (Uncoated $CaCO_3$)	40
Pluronic L-4 PEO/PPO copolymer (drum release/plasticizer)	5

The coating had a good combination of hardness and flexibility such that it could be folded without cracking and it exhibited good release from the casting drum.

Claims

1. A method for providing a coated substrate comprising the steps of:
   (a) providing a radiation or thermally curable coating composition containing less than about 5% solvent or water and containing at least about 60%, and preferably at least about 70%, pigment based on the weight of said composition;
   (b) coating a layer of said coating composition on to at least one surface of a continuous web of a planar substrate as said web is moved past a coating means;
   (c) forming the surface of said layer; and
   (d) at least partially curing said coating composition.

2. A method for forming a printed substrate which comprises the steps of:
   (a) providing a radiation or thermally curable coating composition containing less than about 5% solvent or water and containing at least about 60%, and preferably at least about 70%, pigment based on the weight of said composition;
   (b) coating a layer of said coating composition onto at least one surface of a continuous web of a planar substrate as said web is moved past a coating means;
   (c) forming the surface of said layer;
   (d) at least partially curing said coating composition, and
   (e) applying a printing ink to the surface of said layer.

3. A method according to Claims 1 or 2, wherein said forming step includes contacting the surface of said layer with a casting surface.

4. A method according to Claim 3, wherein said forming step includes contacting the surface of said layer with the surface of a casting drum.

5. A method according to Claim 3, wherein said forming step includes contacting the surface of said layer with the surface of a casting film.

6. A method according to any of Claims 3, 4 or 5, wherein said coating composition is partially cured immediately prior to or during said step of contacting the surface of said layer with said casting surface and said method includes the additional step of more fully curing said composition after said contacting step.

7. A method according to any preceding claim, wherein said coating composition has a viscosity of at least 10,000 cps, and preferably greater than 100,000 cps.

8. A method according to any of Claims 1 to 6, wherein said composition has a viscosity of about 10,000 to 60,000 cps.

9. A method according to any preceding claim, wherein said composition contains no water or solvent.

10. A method according to any preceding claim, wherein said at least partially curing step includes exposing said composition to electron beam radiation.

11. A method according to any preceding claim, wherein said coating composition includes a mixture of monofunctional and polyfunctional monomers or oligomers.

12. A method according to any preceding claim,

13. A method according to any preceding claim, wherein said coating step includes extruding said coating composition on to said at least one surface of said web.

14. A method according to any of Claims 1 to 12, wherein said coating step includes coating said composition on to said at least one surface of said web with an offset gravure roll.

15. A method according to any preceding claim, wherein said composition is coated in an amount of about 7 to 200 gsm.

16. A coated product comprising a substrate having a layer of a coating cured on a surface thereof; characterised in that said cured coating is the result of curing a composition containing less than about 5% solvent or water and from about 70-85% pigment based on the weight of said coating composition, and in that said cured coating has a Sheffield smoothness less than 25.

17. A coated product according to Claim 16, further characterised in that said substrate is paper or paperboard.

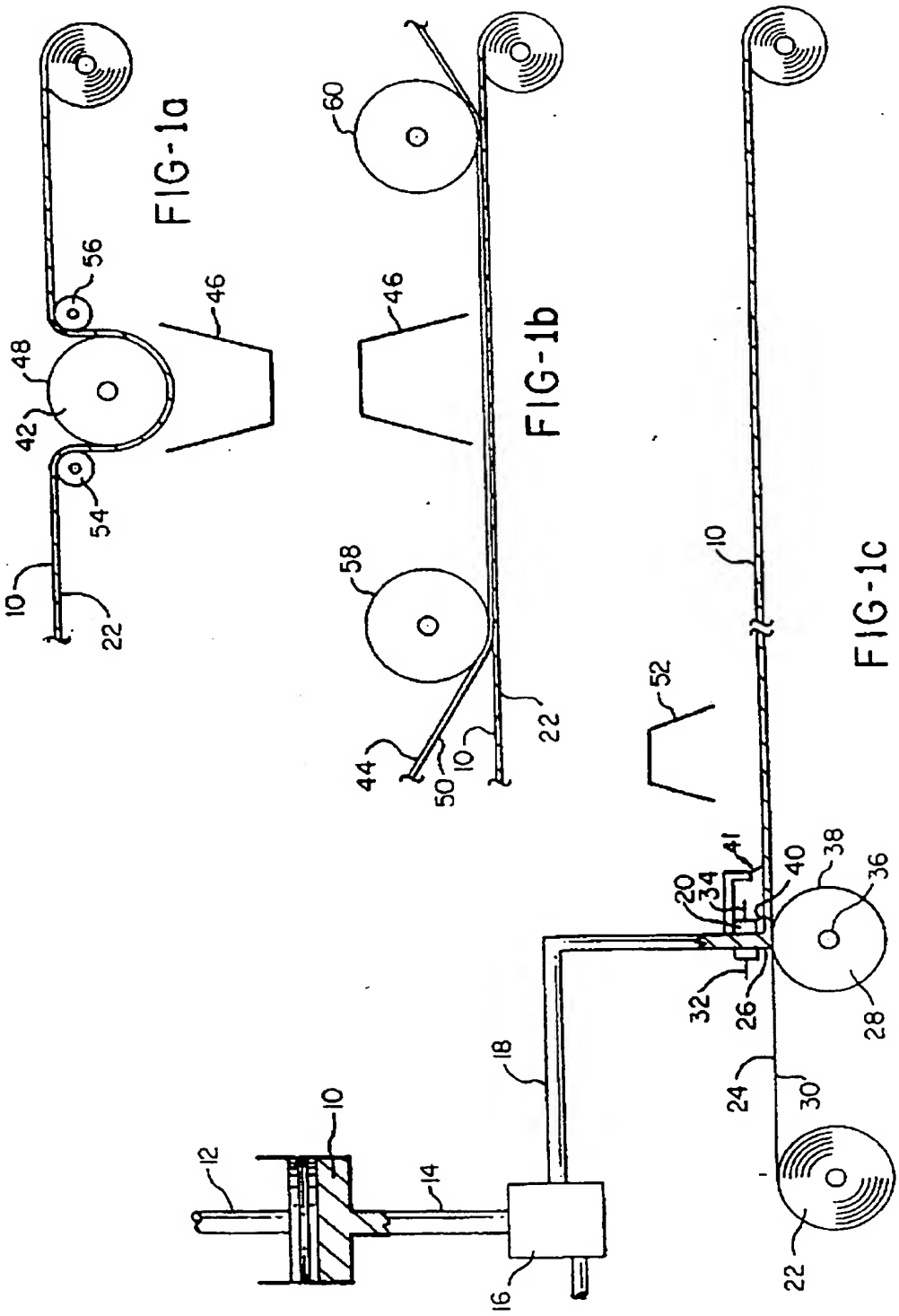
FIG-1a
FIG-1b
FIG-1c
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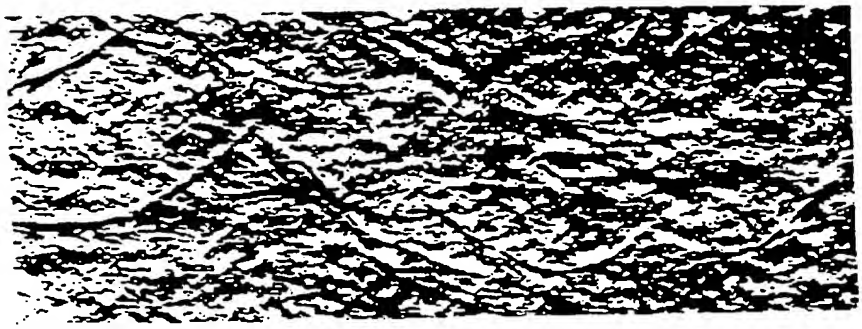
EXAMPLE 2 ON COATED NATURAL KRAFT RAW STOCK

ENERGY SCIENCES, INK DRUM CAST EXAMPLE 2 ON LABEL STOCK MAG. 25X

CAST COATED (CONVENTIONAL)

FIG. 2d



COATED NATUAL KRAFT

RAW STOCK FOR COATED NATUAL KRAFT

FIG 2b

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 31 0380

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-2 524 846 (KANZAKI PAPER) * claims 1-11 *	1-17	B41M5/00 D21H19/48
X	DATABASE JAPIO, n090-243393, ORBIT Search Service, California, US; & JP-A-2243393(MITSUBISHI PAPER) 27-09-90 *The entire abstract*	1-17	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B41M
D21H
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 JANUARY 1992	fouquier

EPO FORM 1503 03.82 (P0401)

CATEGORY OF CITED DOCUMENTS

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